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The Chemistry of Uranium. Part 32. The Electronic Structure of UCl_4 and $ThCl_4$ Complexes of some Neutral Donor Ligands

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Studies of the X-ray photo-electron spectra (XPS) of uranium compounds recently became a useful tool to obtain information about their valence electronic structure [1]. It was indicated that for UF_4 and UCl_4 the 5f electrons are essentially localised on the metal, even in the gas phase [2, 3]. From a comparison between the tetrafluorides and chlorides of uranium and thorium the only significant differences in electronic structure were the presence of 5f electrons in the tetravalent uranium and their absence in thorium. A similar situation occurs in the X-ray photo-electron spectra of solid UO_2 and ThO_2 [4], where except for the existence of a low-lying 5f ionization in UO_2, the ThO_2 and UO_2 valence-band photo-electron spectra are nearly identical. During the recent studies of the XPS of MCl_4L_2 compounds where M = Th and U and L = tris(dimethylamido)phosphine oxide (tdpo) and triphenylarsine oxide (tpao), somewhat surprising results were obtained which indicated the presence of 5f electrons in thorium.

Experimental

Pure MCl_4tdpo_2 and MCl_4tpao_2 (M = U, Th) were synthesised as described previously [5]. The samples (in powder form) were dissolved in the appropriate solvents: nitromethane for UCl_4tdpo_2, dichloromethane for UCl_4tpao_2 and acetone for $ThCl_4tdpo_2$ and $ThCl_4tpao_2$. A thin film was then recrystallised on a gold plate and the sample introduced in this form inside the spectrometer.

The X-ray photo-electron spectra were obtained at room temperature on a AEI200B (Kratos) instrument using non-monochromatized MgKα radiation ($h\nu$ = 1253.6 eV). Although the use of non-monochromatized X-rays and the preparation of the sample in the form of a thin film on a gold plate minimize the positive charge build-up at the surface of insulating material due to the emitted photo-electrons, a slight charging effect was observed for UCl_4tdpo_2. The technique to estimate the extent of charging is based on the evolution of the shift of a peak as a function of the X-ray intensity [6]. The correction for the charging is included in the reported results. Three independent measurements were recorded for each compound and the binding energies (B.E.) quoted are the mean of these three measurements.

The intensity of a peak is measured by the area under a gaussian simulation of the signal. Only relative intensities (intensity ratios) are reported.

Results and Discussion

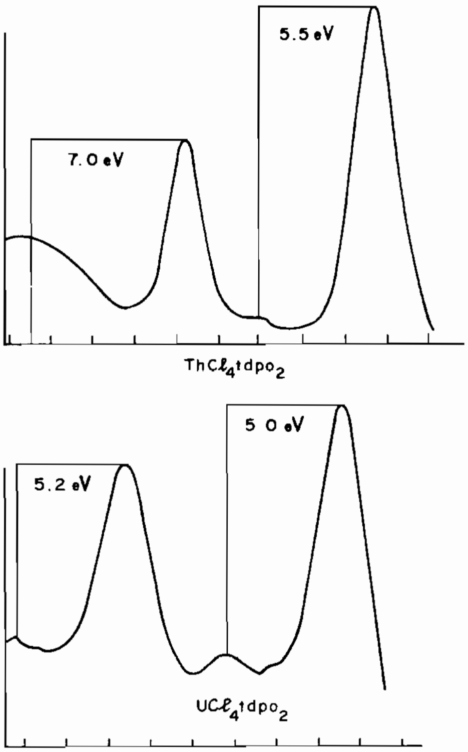

Fig. 1. 4f spectra of $ThCl_4tdpo_2$ and UCl_4tdpo_2.

The 4f spectra of U(IV) and Th(IV) complexes show in addition to the $4f^{7/2}$ and $4f^{5/2}$ peaks a satellite structure understood as a shake-up process (Fig. 1). The satellites observed correspond to a valence electron excitation simultaneously with photo-emission and obey the monopole selection rule. The electronic transition observed corresponds to the excitation of an electron of a molecular orbital with strong ligand character (Cl3p) to an orbital mainly of 5f character based on the metal centre. In this respect, the 4f spectra of the UCl_4L_2 and $ThCl_4L_2$ complexes investigated here are very similar

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TABLE I. Relative Positions and Intensities of Shake-up Satellites in Th4f and U4f Spectra.

	Satellite position in e.V.		Satellite/Parent peak intensity ratio	
	$4f^{5/2}$	$4f^{7/2}$	$4f^{5/2}$	$4f^{7/2}$
$ThCl_4tdpo_2$	7.0	5.5	0.90	0.01
$ThCl_4tpao_2$	6.6	5.6	0.21	0.07
$ThCl_4$ [a]	5.3	5.7	0.13	0.10
UCl_4tdpo_2	5.0	5.2	0.23	0.05
UCl_4tpao_2	–	3.3	–	0.19
UCl_4 [b]	–	6.1	–	0.30

[a] From ref. 7. [b] From ref. 8.

to the ones reported in the literature for UCl_4 and $ThCl_4$ (Table I) [7, 8]. The conclusion is therefore reached that the presence of the organic ligands (L) has little influence on the metal-halide bond. On the other hand, the intensity of the satellite lines is indicative of the 5f admixture in the LUMO (lowest unoccupied molecular orbital). A difference between UCl_4L_2, $ThCl_4L_2$ on the one side and UCl_4 and $ThCl_4$ on the other is distinctly observable (Table I). The contribution of 5f orbitals in the LUMO of the hexacoordinated complexes is apparently reduced, probably because they are involved with the axial ligands L.

The valence region of the XPS spectra also provides insight into the electronic configuration of actinide compounds. In the region of 0.0 to 15.0 eV two bands are generally observed in uranium tetrahalides. The first band (A), closer to the Fermi level, is attributed to the 5f levels while the second one (B) is made-up of U7s, 6d, 5f and halide p character [4, 8]. The valence region of our six-coordinate uranium(IV) complexes differs very little from U tetrahalide spectra, though the intensity of bands A and B are closer to each other in UCl_4L_2 than in UCl_4 itself.

It has been shown [1] that the valence spectra of U(IV) and Th(IV) tetrahalide complexes are very similar, with the difference however that in the thorium compounds the band associated with the metal 5f ionization is not observed. This is explained by the fact that these Th(IV) compounds have a $5f^0$ electronic configuration. However, from a comparison of the valence region of UCl_4L_2 and $ThCl_4L_2$ (Fig. 2) it can be seen that a band very similar to the U5f appears in the spectra of the thorium complexes which is absent in $ThCl_4$ (Table II). It must therefore be concluded that in $ThCl_4L_2$, the 5f orbitals of thorium are no longer empty. It can be assumed that they are populated from the 2p orbitals of the coordinating oxygen atoms of the axial ligands.

This evidence for a covalent character in the Th–O bond of the neutral ligand is in agreement with structural data obtained for a series of UCl_4L_2 complexes in which the degree of tetragonal distortion (U–O bond shortening and corresponding U–Cl bond lengthening) could be correlated with the donor strength of the neutral ligand [9]. In the case of L = triethylarsine oxide the shortest U–O bond (2.16 Å) and longest U–Cl bond (2.665 Å) were obtained as compared to 2.24 Å and 2.618 Å for the analogous bonds in UCl_4tppo_2 (tppo = triphenylphosphine oxide). The above XPS results seem to suggest that very significant covalent character exists between the quadrivalent actinides (U and Th) in those compounds where the coordination number is relatively low, namely six, and the metal is bonded to a readily distortable oxygen atom.

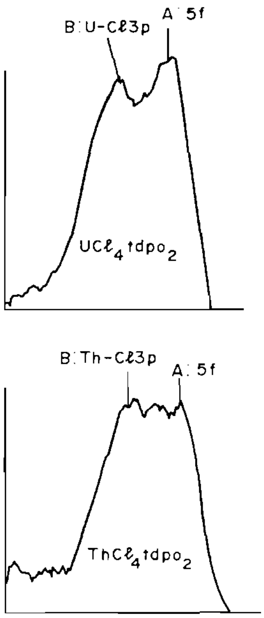

Fig. 2. Valence bands A and B of UCl_4tdpo_2 and $ThCl_4tdpo_2$.

TABLE II. Valence Bands of $ThCl_4L_2$ and UCl_4L_2 Compounds.

	A in e.V.	B	
$ThCl_4tdpo_2$	3.5	5.7	$I_A \simeq I_B$
$ThCl_4tpao_2$	3.7	5.4	$I_A \simeq I_B$
$ThCl_4$ [a]	–	5.7	
UCl_4tdpo_2	3.5	6.0	$I_A > I_B$
UCl_4tpao_2	3.8	5.6	$I_A < I_B$
UCl_4 [b]	1.6	4.4	$I_A > I_B$

[a] From ref. 7. [b] From ref. 8.

Acknowledgements

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